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# Development and Validation of a One-Dimensional Co-electrolysis Model for Use in Large-Scale Process Modeling Analysis

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## ABSTRACT

A one-dimensional chemical equilibrium model has been developed for analysis of simultaneous high-temperature electrolysis of steam and carbon dioxide (coelectrolysis) for the direct production of syngas, a mixture of hydrogen and carbon monoxide. The model assumes local chemical equilibrium among the four process-gas species via the shift reaction. For adiabatic or specified-heat-transfer conditions, the electrolyzer model allows for the determination of coelectrolysis outlet temperature, composition (anode and cathode sides), mean Nernst potential, operating voltage and electrolyzer power based on specified inlet gas flow rates, heat loss or gain, current density, and cell area-specific resistance. Alternately, for isothermal operation, it allows for determination of outlet composition, mean Nernst potential, operating voltage, electrolyzer power, and the isothermal heat requirement for specified inlet gas flow rates, operating temperature, current density and area-specific resistance. This model has been developed for incorporation into a system-analysis code from which the overall performance of large-scale coelectrolysis plants can be evaluated. The one-dimensional co-electrolysis model has been validated by comparison with results obtained from a 3-D computational fluid dynamics model and by comparison with experimental results.

## INTRODUCTION

One potential path to greater energy independence is the production of synthetic liquid fuels. Coelectrolysis of steam and carbon dioxide using a high-temperature electrolysis process can provide a mixture of carbon monoxide and hydrogen, or syngas, which may be supplied as a feed stream to a Fischer-Tropsch process to generate synthetic liquid fuels. This process, if powered by a carbon-free energy source such as nuclear, has the potential to relieve dependence on fossil fuels, without the major infrastructure shift that would be required for a purely hydrogen-based transportation system. Furthermore, if the carbon dioxide source is based on biomass, the entire fuel production and utilization cycle could be carbon-neutral.

This research is an outgrowth of ongoing work at the Idaho National Laboratory on high-temperature steam electrolysis for hydrogen production [1 - 4], funded by the US Department of Energy under the Nuclear Hydrogen

Initiative. High-temperature electrolysis (HTE) is one of two technologies under evaluation for large-scale hydrogen production based on nuclear energy. Advanced high-temperature nuclear reactors have the potential to enable efficient, large-scale, carbon-free hydrogen production [5]. Large-scale nuclear hydrogen production based on water-splitting is already under serious consideration in the short term to supply hydrogen for upgrading of low-quality petroleum resources such as the Athabasca Oil Sands [6]. In the intermediate term, large-scale hydrogen production will be required for the production of synthetic liquid hydrocarbon fuels. In the long term, large-scale hydrogen production may fuel the hydrogen economy.

High-temperature electrolysis is based on solid oxide fuel cell (SOFC) technology and materials. The zirconia electrolytes used for SOFCs conduct oxygen ions, so they can be used to electrolyze  $\text{H}_2\text{O}$  to  $\text{H}_2$  and/or  $\text{CO}_2$  to  $\text{CO}$ . When both steam and carbon dioxide are present simultaneously in the feed stream, the total amounts of hydrogen and carbon monoxide that are produced depend on the electrolysis current. The relative amount of hydrogen produced versus carbon monoxide is determined by the relative amounts of steam, hydrogen (included in the feed stream as a reducing agent) and carbon dioxide included in the feed stream and by the effect of the shift reaction:



The desired molar ratio of hydrogen to carbon monoxide in the gaseous product depends on the particular liquid fuel to be produced as a final product, but a 2-to-1 ratio of  $\text{H}_2$  to  $\text{CO}$  is typical.

In order to evaluate the potential syngas-production performance of large-scale high-temperature coelectrolysis operations, we have developed an engineering process model at INL using the commercial system-analysis code HYSYS. Using this code, several detailed process flow sheets have been defined that include all of the components that would be present in an actual HTCE plant such as pumps, compressors, heat exchangers, turbines, and the electrolyzer. However, since the actual electrolyzer is not a standard HYSYS component, custom one-dimensional coelectrolysis models have been developed for both steam [7] and steam/ $\text{CO}_2$  electrolysis for incorporation into the overall process flow sheet. The one-dimensional coelectrolysis model accounts for the chemical equilibrium of the components via the shift reaction and removal of oxygen from the system via electrolysis.

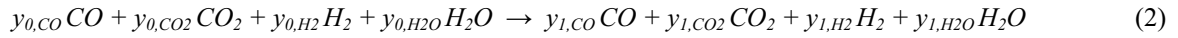
This paper will provide details on the development of the one-dimensional chemical equilibrium coelectrolysis (CEC) model, its implementation in the systems-analysis code, comparisons to computational fluid dynamics (CFD) results, and electrolyzer performance predictions based on the one-dimensional model over a range of operating conditions.

## V. CHEMICAL EQUILIBRIUM MODEL

A one-dimensional chemical equilibrium model has been developed for analysis of steam/carbon dioxide coelectrolysis. This model can be used to predict open-cell and operating potentials, electrolyzer outlet compositions, and outlet temperatures for specified inlet gas flow rates, current densities, cell area-specific resistance, and thermal boundary condition.

The Nernst potential for the coelectrolysis system can be calculated as a function of temperature using the Nernst equation for either steam-hydrogen or for CO<sub>2</sub>-CO, provided the equilibrium composition of the components is used in the evaluating the equation. Therefore, prior to applying the Nernst equation, the electrolyzer-inlet equilibrium composition must be determined at the operating temperature. Our chemical equilibrium coelectrolysis model determines the equilibrium composition of the system as follows.

The overall shift reaction that occurs during heatup from the cold unmixed inlet conditions to the hot mixed pre-electrolyzer state can be represented as:



where the  $y_{0,j}$  values represent the cold inlet mole fractions of CO, CO<sub>2</sub>, H<sub>2</sub>, and H<sub>2</sub>O, respectively, that are known from specification of the individual component inlet gas flow rates. The unknown equilibrium mole fractions of the four species at the electrolyzer temperature, prior to electrolysis, are represented by the  $y_{1,j}$  values. There are three governing chemical balance equations for carbon, hydrogen, and oxygen corresponding to Eqn. (2):

$$y_{0,CO} + y_{0,CO_2} = y_{1,CO} + y_{1,CO_2} \quad (3)$$

$$2y_{0,H_2} + 2y_{0,H_2O} = 2y_{1,H_2} + 2y_{1,H_2O} \quad (4)$$

$$y_{0,CO} + 2y_{0,CO_2} + y_{0,H_2O} = y_{1,CO} + 2y_{1,CO_2} + y_{1,H_2O} \quad (5)$$

The final equation invokes the equilibrium constant for the shift reaction:

$$K_{eq}(T) = \frac{y_{1,CO_2} y_{1,H_2}}{y_{1,CO} y_{1,H_2O}} \quad (6)$$

completing a system of four equations and four unknowns. Simultaneous solution of this system of equations yields the hot inlet composition.

Once the hot inlet equilibrium composition is determined, the open-cell Nernst potential can be calculated from:

$$V_N = \frac{-\Delta G_{f,H_2O}(T)}{2F} - \frac{R_u T}{2F} \ln \left[ \left( \frac{y_{1,H_2O}}{y_{1,H_2} y_{O_2}^{1/2}} \right) \left( \frac{P}{P_{std}} \right)^{-1/2} \right] = \frac{-\Delta G_{f,CO_2}(T)}{2F} - \frac{R_u T}{2F} \ln \left[ \left( \frac{y_{1,CO_2}}{y_{1,CO} y_{O_2}^{1/2}} \right) \left( \frac{P}{P_{std}} \right)^{-1/2} \right] \quad (7)$$

where  $y_{O_2}$  is the mole fraction of oxygen on the air-sweep side of the cells ( $y_{O_2} \sim 0.21$ ). Note that the Nernst equation for either steam-hydrogen or  $CO_2$ -CO yields the same result for the equilibrium system.

The electrolyzer outlet composition can be determined similarly, after accounting for electrochemical reduction of the system. The chemical balance equation for oxygen must be modified to account for oxygen removal from the  $CO_2$ /steam mixture. Accordingly, the oxygen balance equation becomes:

$$y_{1,CO} + 2y_{1,CO_2} + y_{1,H_2O} = y_{2,CO} + 2y_{2,CO_2} + y_{2,H_2O} + \Delta n_O \quad (8)$$

where  $\Delta n_O$  is the relative molar rate of monatomic oxygen removal from the  $CO_2$ /steam mixture given by:

$$\Delta n_O = \frac{I_e}{2F\dot{N}_{Tot}} \quad (9)$$

In this equation,  $I_e$  is the total ionic current,  $I_e = i \cdot A_{cell} \cdot N_{cells}$ ,  $\dot{N}_{Tot}$  is the total molar flow rate on the  $CO_2$ /steam side, including any inert gas flows, and  $F$  is the Faraday number. Finally, using the modified oxygen balance equation, the post-electrolyzer equilibrium composition (state 2) can be determined as a function of temperature from simultaneous solution of three chemical balance equations and the equilibrium constant equation.

In general, the electrolyzer outlet temperature is unknown. The magnitude of any temperature change associated with electrolyzer operation depends both on the operating conditions (operating voltage, inlet composition, gas flow rates, etc.) and on the thermal boundary condition. If the electrolyzer operating voltage is below the thermal neutral voltage, the endothermic reaction heat requirement dominates and the stack will tend to cool off. If the operating voltage is above thermal neutral, ohmic heating dominates and the stack tends to heat up.

If adiabatic electrolyzer operation is assumed, the outlet temperature can be determined as a function of operating voltage from simultaneous solution of the energy equation and the chemical balance and equilibrium constant equations. Alternately, if isothermal operation is assumed, the outlet composition can be determined

independently of the energy equation and the heat required to maintain isothermal operation can be calculated as a function of operating voltage.

For pure-steam or pure-CO<sub>2</sub> electrolysis, the thermal neutral voltage is given by

$$V_{m,j}(T) = \frac{\Delta H_{R,j}(T)}{2F} \quad (10)$$

where  $\Delta H_{R,j}(T)$  is the enthalpy of reaction for electrolysis of pure component  $j$  (H<sub>2</sub>O or CO<sub>2</sub>) at temperature  $T$ . At 800°C,  $V_{m,H_2O} = 1.29$  V and  $V_{m,CO_2} = 1.46$  V. For coelectrolysis, the thermal neutral voltage can range anywhere between the respective pure-component values, depending on inlet composition, oxygen utilization, and temperature (via the equilibrium constant,  $K_{eq}(T)$ ). There is no simple explicit relation for the multi-component thermal neutral voltage. In general, the thermal neutral voltage for coelectrolysis will be closer to the pure-steam value if the inlet composition is dominated by steam and hydrogen. Conversely, if the inlet composition is dominated by CO<sub>2</sub> and CO, the coelectrolysis thermal neutral voltage will be closer to the pure-CO<sub>2</sub> value. At an operating temperature of 800°C, with syngas-production-relevant inlet compositions for coelectrolysis (i.e., ~2-to-1 steam/hydrogen vs CO<sub>2</sub>), a thermal neutral voltage value of ~1.34 V is typical.

The energy equation for the coelectrolysis process can be written as:

$$\dot{Q} - \dot{W} = \sum_P \dot{N}_i [\Delta H_{f,i}^o + H_i(T_P) - H_i^o] - \sum_R \dot{N}_i [\Delta H_{f,i}^o + H_i(T_R) - H_i^o] \quad (11)$$

where  $\dot{Q}$  is the external heat transfer rate to or from the electrolyzer,  $\dot{W}$  is the rate of electrical work supplied to the electrolyzer,  $\dot{N}_i$  is the molar flow rate of each reactant or product,  $\Delta H_{f,i}^o$  is the standard-state enthalpy of formation of each reactant or product and  $H_i(T) - H_i^o$  is the sensible enthalpy for each reactant or product. Applying the energy equation in this form, all reacting and non-reacting species in the inlet and outlet streams are accounted for, including inert gases, process steam, hydrogen (introduced to maintain reducing conditions on the steam/hydrogen electrode), CO<sub>2</sub>, and any excess unreacted process gases.

In general, determination of the outlet temperature from Eqn. (11) is an iterative process. The heat transferred during the process must first be specified (e.g., zero for the adiabatic case). The temperature-dependent enthalpy values of all species must be available from curve fits or some other data base. The cathode-side hot electrolyzer-inlet molar composition and flow rates of steam, hydrogen, CO<sub>2</sub>, CO, and any inert carrier gases such as nitrogen (if applicable) have already been determined from specification of the cold inlet flow rates of all components and from

Eqns. (2 – 6). The inlet flow rate of the sweep gas (e.g., air or steam) on the anode side must also be specified. At this point, the total electrolyzer-inlet enthalpy given by the second summation on the right-hand side of Eqn. (11) can be evaluated.

The current density, active cell area, and number of cells are then specified, yielding the total ionic current,  $I_e$ . Care must be taken to insure that the specified inlet gas flow rates and total ionic current are compatible. The minimum required inlet steam and CO<sub>2</sub> molar flow rates must satisfy the following constraint:

$$\dot{N}_{H_2O} + \dot{N}_{CO_2} \geq \frac{I_e}{2F} \quad (12)$$

to avoid oxygen starvation. Note that the oxygen contribution from the CO<sub>2</sub> is only counted once, since we want to avoid creation of carbon soot, which could foul the cells.

Evaluation of the electrolyzer-outlet total enthalpy, the first summation in Eqn. (11), requires the product temperature, but the product temperature is generally unknown and is determined from solution of the energy equation, so an iterative solution must be applied. The iterative solution process proceeds as follows. Based on a guessed value of electrolyzer outlet temperature,  $T_p$ , and the specified current, the electrolyzer outlet composition can be determined as described previously, allowing for evaluation of the total enthalpy of the products.

The remaining term in the energy equation is the electrical work, which is the product of the per-cell operating voltage and the total ionic current. The operating voltage corresponding to the specified current density is obtained from:

$$V_{op} = \bar{V}_N + i \times ASR(T) \quad (13)$$

The stack area-specific resistance,  $ASR(T)$ , quantifies the loss mechanisms in the operating cell. It must be estimated, based on experimental data or an appropriate model, and specified as a function of temperature. The operating-cell mean Nernst potential,  $\bar{V}_N$ , accounting for the variation of gas composition and temperature across the operating cell, can be obtained from an integrated form of the steam-hydrogen-based (or the CO<sub>2</sub>-CO-based) Nernst equation:

$$\bar{V}_N(T_P) = \frac{1}{2F(T_P - T_R)(y_{2,O_2} - y_{1,O_2})(y_{2,H_2}(T_P) - y_{1,H_2})} \times$$

$$\int_{T_R}^{T_P} \int_{y_{1,O_2}}^{y_{2,O_2}} \int_{y_{1,H_2}}^{y_{2,H_2}(T_P)} \Delta G_{R,H_2O}(T) + R_u T \ln \left( \frac{1 - y_{H_2} - y_{O_2} - y_{N_2}}{y_{H_2} y_{O_2}^{1/2}} \right) dy_{H_2} dy_{O_2} dT \quad (14)$$

Note that the variable in this equation is the unknown product temperature,  $T_P$ , which appears both explicitly and implicitly in the upper integration limits. The steam mole fraction has been expressed in the integrand numerator in terms of the hydrogen mole fraction. The mole-fraction subscripts 0, 1, 2 again refer to the cold inlet, hot electrolyzer inlet, and the hot electrolyzer outlet states, respectively. Mole fractions at states 0 and 1 are fully defined. The state-2 mole fractions are based on the specified current density and the guessed value for  $T_P$ .

Once the mean Nernst potential is evaluated based on a guessed value for  $T_P$ , the operating voltage can be determined and the energy equation can be evaluated. The final converged solution for  $T_P$  must simultaneously satisfy the chemical balance Eqns. (3, 4, 8), the equilibrium constant Eqn. (6), and the energy Eqn. (11), subject to Eqns. (13 – 14).

The solution methodology described above can be applied to any specified electrolyzer heat loss or gain. For adiabatic operation,  $Q = 0$ . Alternately, if the heat loss or gain from the operating electrolyzer is known from a separate heat transfer analysis for a given operating point, the value of that heat loss or gain would be used.

For isothermal electrolyzer operation, once the inlet flow rates, current density, and operating temperature are specified, an iterative solution is not necessary and the triple integral of Eqn. (14) reduces to a double integral with known upper limits of integration. The energy Eqn. (11) can be solved directly for the heat required to maintain isothermal operation at any operating point.

The CEC model allows for accurate determination of coelectrolysis outlet temperature, composition (anode and cathode sides), mean Nernst potential, operating voltage and electrolyzer power based on specified inlet gas flow rates, heat loss or gain, current density, and cell  $ASR(T)$ . Alternately, for isothermal operation, it allows for determination of outlet composition, mean Nernst potential, operating voltage, electrolyzer power, and the isothermal heat requirement for specified inlet gas flow rates, operating temperature, current density and  $ASR(T)$ . The model was initially implemented analytically in MathCad.

## IMPLEMENTATION OF THE COELECTROLYSIS MODEL IN HYSYS

The CEC model was developed for comparison to experimental results [8, 9] and also for incorporation into system-level electrolysis plant models being developed using HYSYS [10] system simulation software. With a



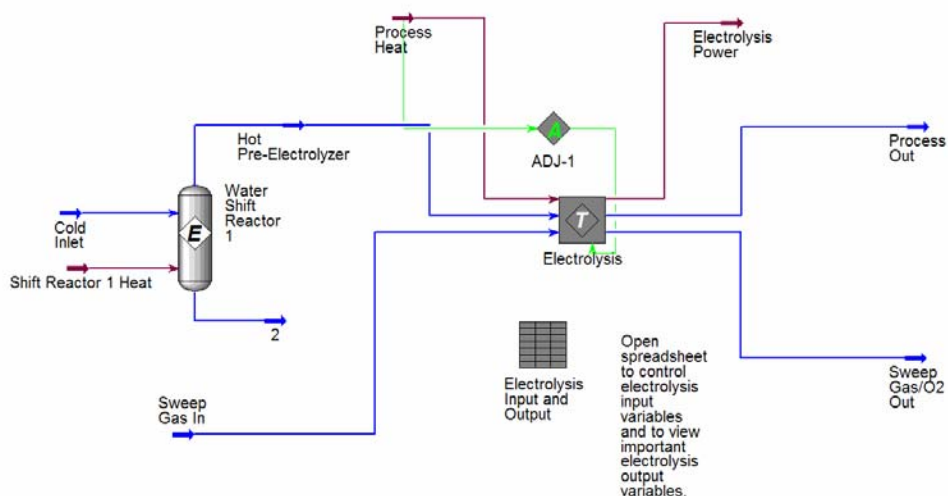


Figure 1. Process flow diagram of the chemical equilibrium coelectrolysis model in HYSYS.

realistic coelectrolysis model incorporated into the overall HYSYS plant model, estimates of overall plant syngas-production efficiencies can be obtained over a wide range of prospective operating conditions.

Implementation of the CEC model in HYSYS was done in a way that took advantage of as many built-in features of the systems-analysis code as possible. Fig. 1 provides a process flow diagram (PFD) representing the implementation of the CEC model in HYSYS. The user-specified cold inlet process-gas stream enters at the left. This stream is equilibrated at the desired electrolyzer inlet temperature by means of an equilibrium reactor module that supports the shift reaction, Eqn. (1). The hot shifted stream and the heated sweep-gas stream enter the electrolysis module. This electrolysis module was developed previously for pure steam electrolysis [11]. At this level of the model, the user may specify whether the electrolysis process will be isothermal or adiabatic. If the process is isothermal, the temperature of the process outlet stream must be specified, otherwise, the outlet temperature is determined by iteration using an embedded adjust logical (shown as the A within the diamond) until the process heat is zero. Also at this level, an embedded spreadsheet is used to input the electrolysis variables, (i.e. current density, number of cells, cell area, area specific resistance, etc.).

The process flow diagram for the electrolysis module is shown in Fig. 2. The hot shifted process stream enters a conversion reactor where the steam and/or carbon dioxide are electrolytically reduced. The conversion reactor unit includes both the steam and carbon dioxide reduction reactions. Based on the percent conversion of the steam and CO<sub>2</sub>, the reactor will calculate the heat of reaction. The percent conversion of steam and/or CO<sub>2</sub> is determined by the amount of oxygen generated using Eqn. (9). This value of the molar flow rate of produced oxygen is stored in a dummy stream. A logical adjust is used to change the percent conversion of steam and carbon dioxide until the

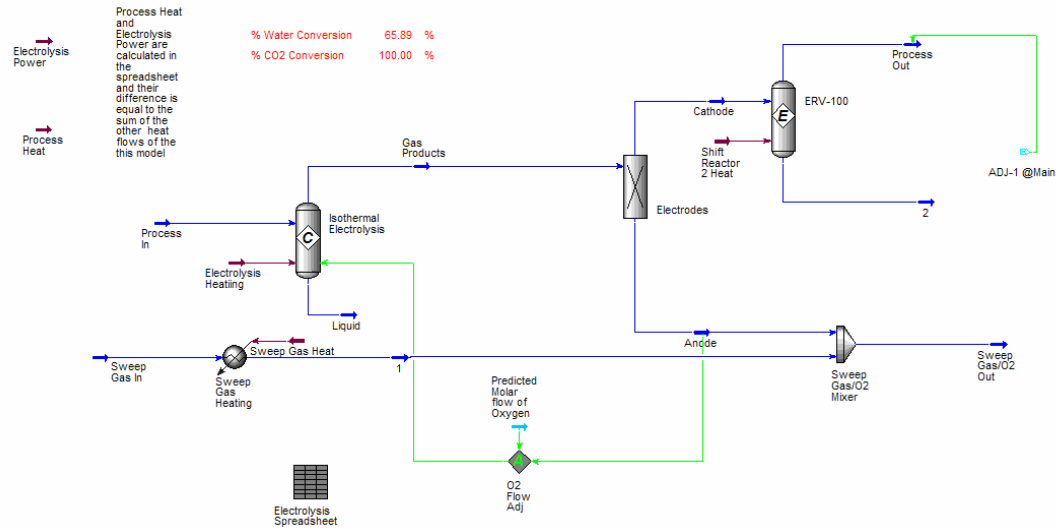


Figure 2. Process flow diagram for the electrolysis module within HYSYS.

oxygen molar flow rate leaving the conversion reactor is the same as the calculated value. The oxygen is split from the rest of the reacted process-gas components by means of a component splitter unit (labeled Electrodes). The split oxygen combines with the sweep gas. The remaining components are passed through a second shift reactor to determine the outlet equilibrium composition.

As previously mentioned, the outlet temperature of both the process and sweep streams are specified but allowed to adjust if adiabatic conditions are desired. An embedded spreadsheet is used to evaluate the mean Nernst potential, Eqn. (14). Assuming a functional relationship for the Gibbs energy of formation, the definite integral was simplified analytically and this simplified version was programmed into the spreadsheet. The HYSYS calculation proceeds as follows: having defined the electrolysis variables, the amount of oxygen production is calculated in the spreadsheet using Eqn. (9). Based on an assumed outlet temperature, HYSYS proceeds to calculate all the thermodynamics and chemical reactions of the process resulting in outlet compositions for the process and sweep streams. With these now defined, the spreadsheet can calculate the mean Nernst potential by evaluating the simplified triple integral, Eqn. (14). The operating voltage is obtained from Eqn. (13) and the electrolysis power is calculated by multiplying the operating voltage with the total current. HYSYS inherently assures that the energy balance, Eqn. (11) is satisfied, which allows the process heat to be calculated by summing the electrolysis power with the total enthalpy differences from the electrolysis process and from the second shift reactor. If the outlet temperature is specified to be the same as the inlet temperature (isothermal operation), the calculation is complete

and the process heat is known. If the process is specified to be adiabatic, the outlet temperature is adjusted until the process heat is zero. The process flow sheet automatically assures mass and energy balances.

## RESULTS

Representative results obtained using both the MathCad and HYSYS implementations of the one-dimensional coelectrolysis model will now be discussed, with comparisons to three-dimensional computational fluid dynamic results. Electrolyzer-outlet mole fractions of the four process-gas species are presented in Fig. 3 as a function of current density for the per-cell inlet molar flow rates, inlet temperature, area-specific resistance, and thermal boundary condition indicated in the figure. The cold inlet moles fractions corresponding to the indicated molar flow rates are also indicated in the figure for each species. Outlet mole fraction results obtained from the MathCad and HYSYS implementations of the CEC are plotted, along with results obtained from a 3-D CFD coelectrolysis simulation obtained using FLUENT. Details of the FLUENT coelectrolysis model are provided in reference [12]. The FLUENT model includes reaction kinetics via separate forward and backward reaction rate constants for the shift reaction. Outlet mole fraction predictions based on the three independent methods are virtually identical. Mole fractions of steam and carbon dioxide decrease with current density, while the mole fractions of hydrogen and

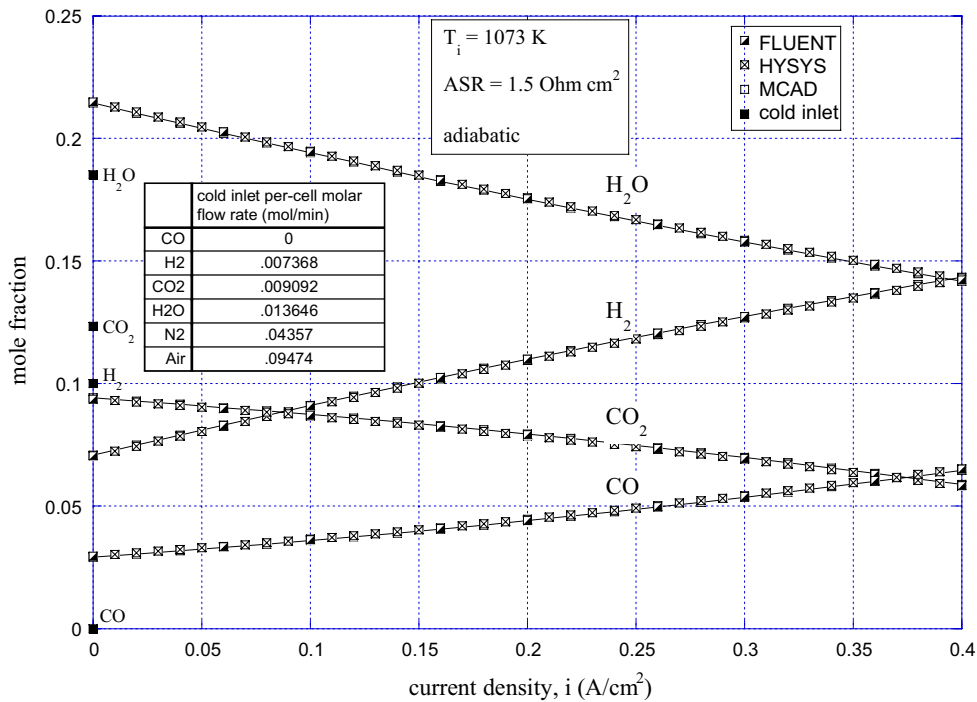


Figure 3. Variation of species mole fraction as a function of current density.

carbon monoxide increase. For the inlet composition chosen for this particular run, the ratio of produced hydrogen to carbon monoxide is slightly higher than 2-to-1.

Calculated final equilibrium compositions have been compared to experimental results obtained from both single-cell and coelectrolysis stack tests. Details of the experimental apparatus and results are provided in references [8, 9]. Comparisons to stack results will be presented here. Measurements of electrolyzer outlet composition were obtained with a downstream dewpoint sensor for steam and with a gas chromatograph for the other gases. However, since these downstream gas composition measurements were obtained at near-room temperatures, these measured compositions are not necessarily expected to agree with predicted outlet compositions evaluated at the furnace temperature. During cool-down from the furnace temperature to room temperature, the gas composition can change, in accordance with the temperature dependence of the shift-reaction equilibrium constant. The magnitude of the composition shift is dependent on cooling rate, presence or absence of catalyst, etc. In general, rapid cooling yields cold outlet compositions that are close to the hot outlet values.

A comparison of experimental results and predictions from the CEC model is presented in Fig. 4. This figure presents the variation in process-gas mole fractions as a function of electrolysis current. The data symbols in the figure indicate measured mole fractions obtained using a gas chromatograph (GC). The GC samples are drawn from

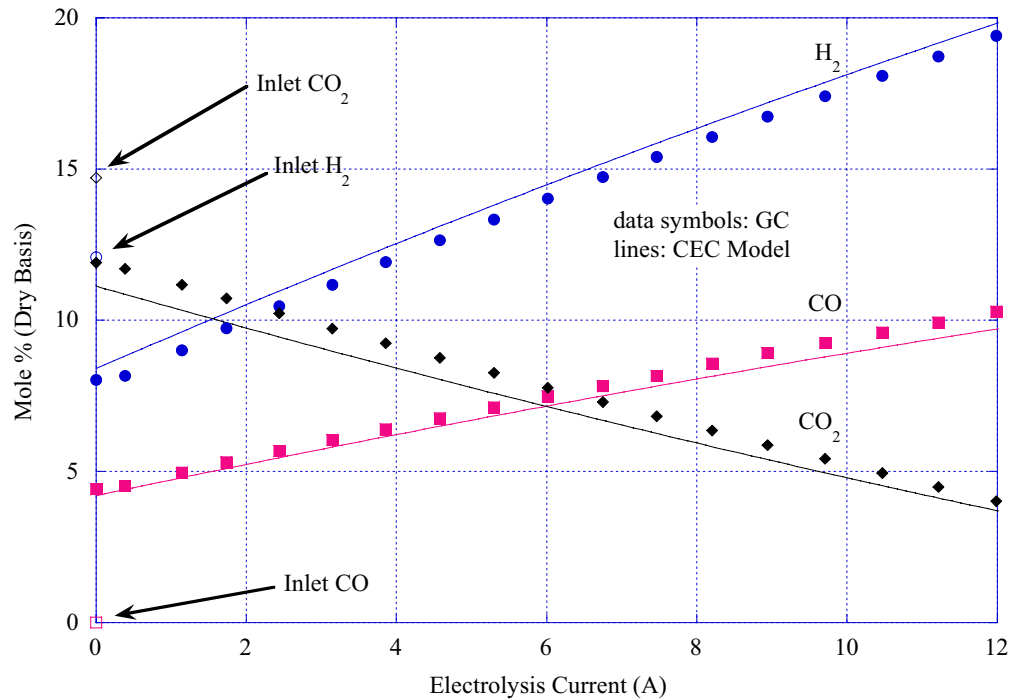


Figure 4. Comparison of measured and predicted coelectrolysis outlet compositions.

the process-gas outlet stream at essentially room temperature and are obtained on a dry basis. The solid lines in the figure represent predictions from the CEC model, evaluated at the electrolyzer outlet temperature, 830°C in this case. The CEC model predictions are quite close to the measured values, despite the fact that the GC measurements were obtained at room temperature.

Electrolyzer outlet temperature predictions from the CEC and FLUENT models are presented in Fig. 5 for the same conditions as the results presented in Fig. 3. For low values of operating voltage (and current density), outlet gas temperatures for adiabatic operation are lower than the inlet temperature. The magnitude of this adiabatic temperature depression is dependent on the voltage and the flow rates of the process gases and sweep gas. For operating voltages higher than the thermal neutral voltage (1.34 V in this case), the gas outlet temperatures are higher than the inlet temperature due to the dominance of ohmic heating. The figure shows predictions from the MathCad and HYSYS versions of the CEC model as well as predictions from the FLUENT model. The 3-D FLUENT model simulates a single electrolysis cell as it would exist in a planar stack, with a cross-flow arrangement of process and sweep gases. Consequently, the average process-gas and sweep-gas outlet temperatures are not necessarily the same. For this particular case, the outlet temperature of the air sweep was higher than the outlet

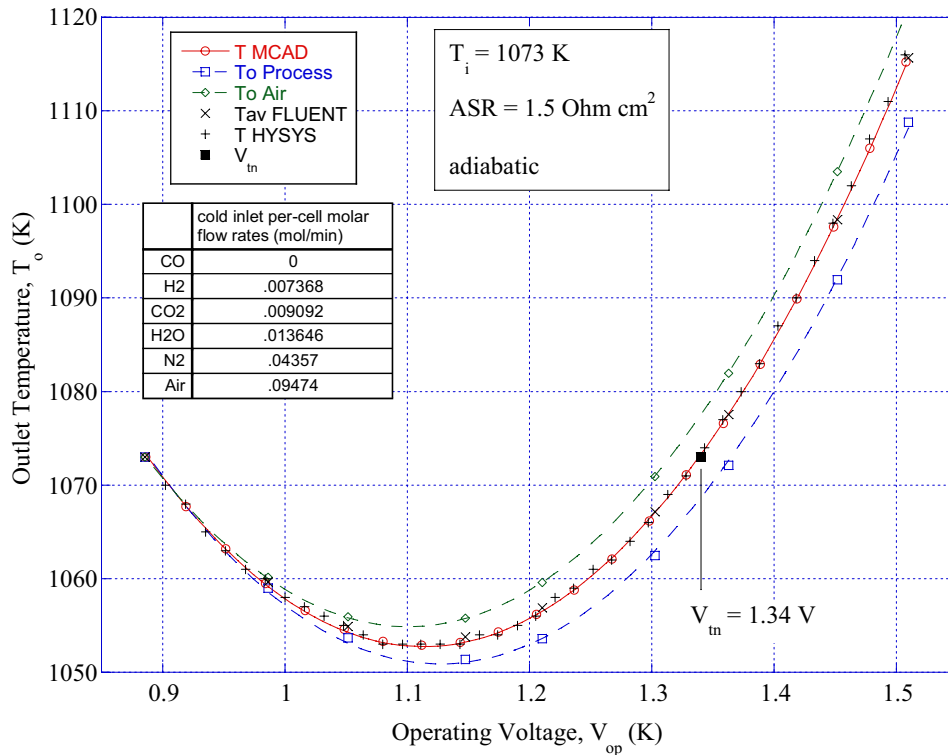


Figure 5. Electrolyzer outlet temperature as a function of operating voltage.

temperature of the process gas, as shown in the figure. An overall heat-capacity-rate-weighted mean outlet gas temperature was also calculated based on the process-gas and sweep-gas flow rates and temperatures. This result is also shown in Fig. 5. The weighted mean outlet temperature agrees very well with predictions obtained from the CEC model.

### Parametric Studies

The CEC model can also be used to perform parametric studies of electrolyzer performance. For example, the effect of area-specific resistance on stack performance can be evaluated. In general, lower  $ASR$  values allow for achievement of a specified current density, and corresponding syngas production rate, at a lower operating voltage and therefore higher electrolysis efficiency [4]. Accordingly, the  $ASR$  value also affects the cell and stack thermal performance. Gas outlet temperatures predicted for adiabatic operation using the CEC model are presented in Fig. 6 as a function of operating voltage for three  $ASR$  values. Cold inlet gas flow rates for these cases are indicated in the figure. Outlet temperatures for the  $ASR = 0.5 \text{ Ohm}\cdot\text{cm}^2$  case decrease dramatically with operating voltage, with a minimum value of 1026.6 K at an operating voltage of 1.112 V. Note that the temperature distribution is parabolic

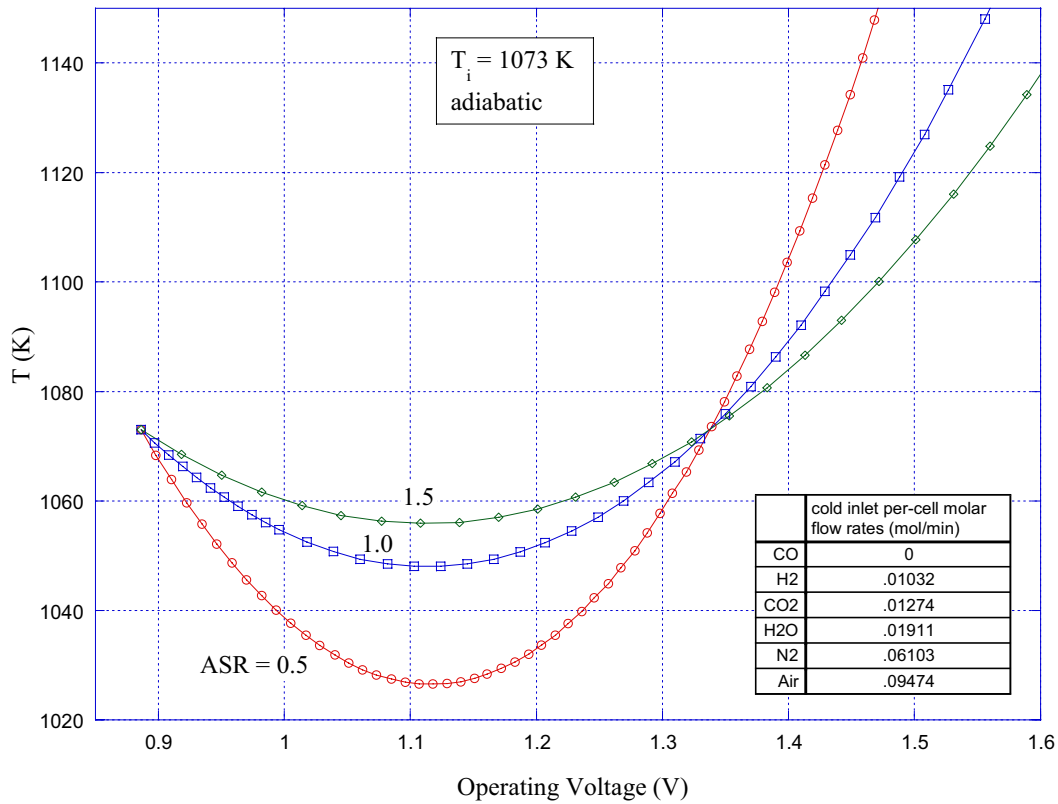


Figure 6. Effect of area-specific resistance on electrolyzer outlet temperature for adiabatic operation.

and that the temperature minimum occurs at an operating voltage that is exactly halfway between the open-cell potential (0.8863 V) and the thermal neutral voltage (1.338 V). For higher operating voltages, outlet temperatures increase and eventually exceed the inlet value for voltages higher than  $V_{tn}$ , above which ohmic dissipation dominates over the endothermic reaction heat requirement. Temperature distributions for the higher ASR values are similar, with smaller variations in magnitude.

Heat transfer requirements predicted for isothermal operation using the CEC model are presented in Fig. 7 as a function of operating voltage for the same three  $ASR$  values. Heat addition (positive heat transfer) is required to maintain isothermal conditions for operating voltages between the open-cell potential and the thermal neutral voltage. Note that the thermal neutral point is the same whether adiabatic or isothermal operation is assumed and that it is independent of  $ASR$ . Heat rejection (negative heat transfer) is required to maintain isothermal operation for operating voltages greater than thermal neutral.

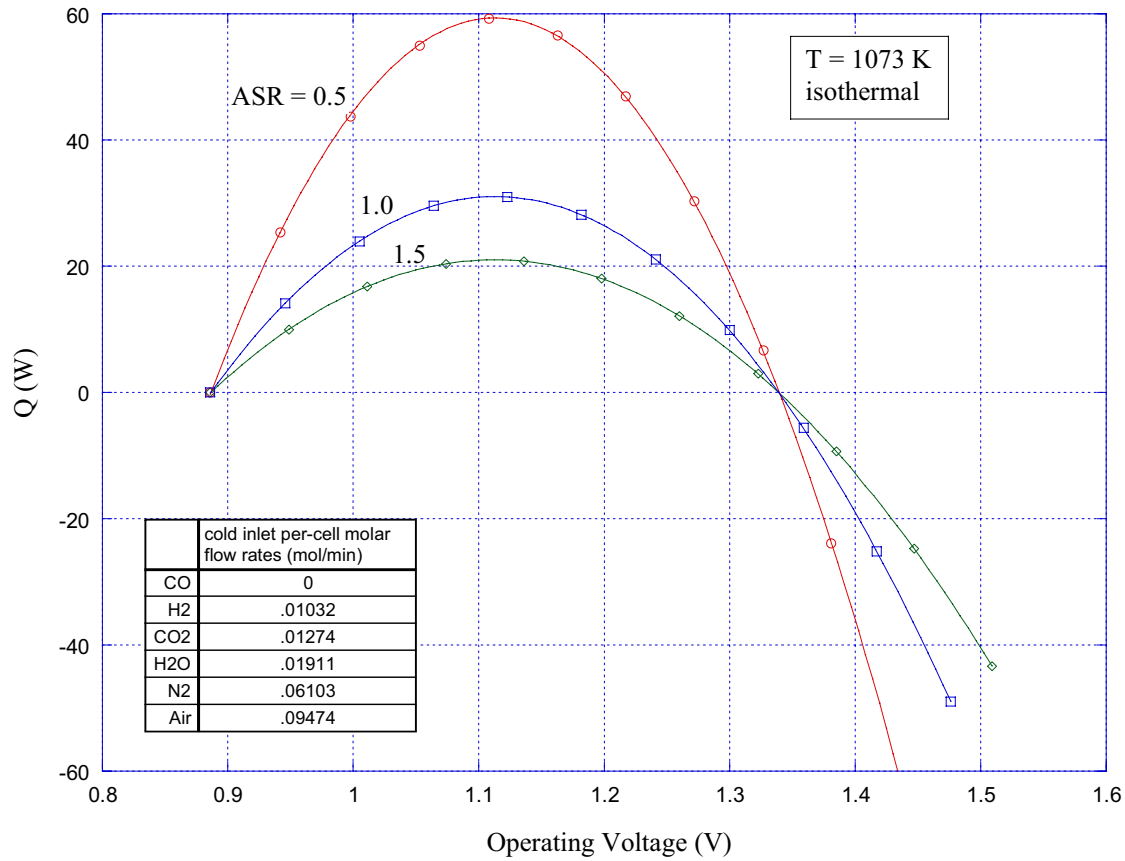


Figure 7. Effect of area-specific resistance on electrolyzer heat transfer for isothermal operation.

## CONCLUSIONS

Coelectrolysis of steam and carbon dioxide using a high-temperature electrolysis process can provide a mixture of carbon monoxide and hydrogen, or syngas, which may be supplied as a feed stream to a Fischer-Tropsch process to generate synthetic liquid fuels. Development of a one-dimensional chemical equilibrium coelectrolysis (CEC) model has been described. The model was implemented analytically in MathCad and later incorporated into HYSYS system analysis software as a custom component. The model assumes local chemical equilibrium among the four process-gas species via the shift reaction. For adiabatic or specified-heat-transfer conditions, the electrolyzer model allows for the determination of coelectrolysis outlet temperature, composition (anode and cathode sides), mean Nernst potential, operating voltage and electrolyzer power based on specified inlet gas flow rates, heat loss or gain, current density, and cell area-specific resistance. Alternately, for isothermal operation, it allows for determination of outlet composition, mean Nernst potential, operating voltage, electrolyzer power, and the isothermal heat requirement for specified inlet gas flow rates, operating temperature, current density and area-specific resistance. The CEC model has been validated by comparison with results obtained from a 3-D CFD model and by comparison with experimental results. Predictions of outlet compositions and temperature obtained from both the MathCad and HYSYS implementations of the CEC as a function of electrolyzer current were virtually identical to results obtained from the 3-D CFD FLUENT simulation. CEC model predictions were also validated by comparison to experimentally measured values. The CEC model can also be used for parametric studies of electrolyzer operation, such as the effect of ASR on gas outlet temperature under adiabatic operation.

## NOMENCLATURE

$A_{cell}$	electrolysis cell active area, $\text{cm}^2$
$ASR$	area-specific resistance, $\text{Ohm}\cdot\text{cm}^2$
$F$	Faraday number, 96487 C/mol
$\Delta G_{f,j}(T)$	Gibbs energy of formation, component j, J/mol
$H_i(T) - H_i^\circ$	sensible enthalpy, component i
$\Delta H_{R,j}(T)$	enthalpy of reaction for steam or CO2 electrolysis, J/mol
$\Delta H_{f,i}^\circ$	enthalpy of formation for component i, J/mol
$I_e$	total ionic current, A
$K_{eq}(T)$	equilibrium constant for shift reaction
$\dot{N}$	molar flow rate, mol/s
$N_{cells}$	number of cells in electrolysis stack
$P$	pressure, kPa
$\dot{Q}$	heat transfer rate to or from electrolyzer, W
$R_u$	universal gas constant, J/K·mol
$T$	temperature, K



$V_N$	Nernst voltage, V
$V_{op}$	operating voltage, V
$V_{in}$	thermal neutral voltage, V
$\dot{W}$	electrical power to electrolyzer, W
$y_{0,j}$	cold inlet mole fraction, component j
$y_{1,j}$	hot electrolyzer-inlet mole fraction, component j
$y_{2,j}$	hot electrolyzer-outlet mole fraction, component j

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